Electrical Characteristics of Anatase-TiO₂ Films by Low Temperature Fabrication

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1. Introduction

It has been reported that CMOS fabricated by the gate-last process at a low temperature are being mass produced. Future scaling of CMOS technology requires a higher-k dielectrics (k >30). Several approaches have been reported to obtain cubic-HfO₂ with a high k value by specific annealing process with fast ramping-up [1, 2]. TiO₂ is one of the most promising candidates of higher-k materials because of a high k value and low temperature crystallization. In this paper, we present characterization of anatase-TiO₂ films fabricated by ALD and PDA processes, and discuss the Vfb change due to oxygen transfer in TiO₂ film by annealing in oxidation and reduction conditions.

2. Experimental

The TiO₂ films with 3-6 nm thicknesses were deposited on SiO₂/Si(100) and SiO₂/Si(111) by the ALD process at 200 °C using Ti(NMe₂)₄ precursor and H₂O gas. The PDA was performed at 300-500 °C for 30 sec in O₂. TiO₂ MOS capacitors with TaC and Pt gate electrodes were fabricated. MOS capacitors with Al₂O₃ and HfO₂ dielectrics were also prepared to discuss the Vfb shift. All capacitors were annealed at 400 °C in 3% H₂ (FGA). The oxygen transfer in TiO₂ layer was controlled by using the catalytic effect of the Pt as follows: To remove oxygen from TiO₂ layer, FGA was carried out at 400-500 °C in 3% H₂. To introduce oxygen into TiO₂ layer, oxidation annealing (ODA) was performed at 100-300 °C for 1-200 min in O₂.

3. Results and Discussion

3.1 Physical characterizations of TiO₂ films

The peaks of C and N impurities in as-deposited TiO₂ film are undetectable by angle-resolved XPS analysis, as shown in Fig. 1. The typical XRD patterns of as-deposited and annealed TiO₂ films are shown in Fig. 2. We found that the TiO₂ film consists of anatase structure at temperature above 300 °C. Fig. 3 shows capacitance equivalent thickness (CET) as a function of TiO₂ thickness on Si(100) and Si(111). The anatase-TiO₂ films were prepared by PDA at 500 °C. The k values in Si(100) and Si(111) samples are estimated 35 and 32, respectively. This demonstrates that the anatase-TiO₂ films which formed at low annealing temperature (500 °C) show a significant high k value (>30).

3.2 Vfb shift due to oxygen transfer in TiO₂ layer

Fig. 4 shows C-V characteristics of TaC-gated MOS capacitors with SiO₂, TiO₂, HfO₂ and Al₂O₃ dielectrics. The C-V curve of TiO₂ capacitor slightly shifts toward positive direction in comparison with SiO₂ capacitor. Fig. 5 summarizes Vfb behaviors of several high-k dielectrics. All high-k dielectrics occurs positive Vfb shift compared with SiO₂. Note that the value of the positive Vfb shift in high-k dielectrics can be ordered as follows: Al₂O₃ (0.72 V) > HfSiO₃ (0.36 V) > HfO₂ (0.29 V) > TiO₂ (0.08 V). It is well known that the Vfb shift of high-k CMOS predominantly occurs due to the bottom interface dipole at high-k/SiO₂ interface [4, 5]. A schematic illustration of band diagram of TaC/high-k/SiO₂/Si stack structure is shown in Fig. 6. The Vfb shift of each dielectric relates to the strength of the bottom interface dipole of each one.

Fig. 7 shows the relationship between the normalized Vfb and the ODA temperature for TiO₂ MOS capacitors with Pt and TaC gate electrodes. The Vfb of the Pt-gated MOS capacitors shifts in the positive direction as the ODA temperature increases, while the Vfb of TaC-gated MOS capacitors shows an almost constant value. No difference of the V-C curve and Vfb behaviors between Si(100) and Si(111) samples appears regardless of the ODA temperature. This indicates that the orientation of Si substrate doesn’t affect to the Vfb shift. To investigate the influence of the oxygen transfer in the TiO₂ layer on the Vfb shift, we examined the annealing time dependence of the Vfb shift, as shown in Fig. 8. The C-V curves of capacitor shift in the positive direction with increasing the annealing time (an inset graph). The Vfb change in ODA at 250 °C saturates at ODA times above 4 min. In contrast, none of the Vfb value in ODA at 150 °C is saturated even after annealing for 200 min. These results suggest that the oxygen diffusion in TiO₂ layer affects to the Vfb shift as previously reported [6]. Fig. 9 shows the change of Vfb for TiO₂, HfO₂ [6] and HfSiO₃ [6] dielectrics after ODA at 300 °C and FGA at 500 °C. The positive and negative Vfb shifts for all samples appear in ODA and FGA treatments, respectively. We found that the TiO₂ dielectric shows the maximum and minimum Vfb change after ODA and FGA, respectively. This strongly indicates that the oxygen transfer of the TiO₂ dielectric is faster than those of HfO₂ and HfSiO₃ dielectrics.

4. Conclusions

We demonstrate that anatase-TiO₂ films, which formed in low temperature fabrication process, show a significant high dielectric constant of 35. We found that the Vfb of TiO₂ capacitor shifts slightly toward positive direction in comparison of SiO₂. Note that the oxygen transfer in TiO₂ layer relates to the Vfb shift from results in ODA and FGA.

References

Fig. 1. Angle-resolved XPS spectra of (a)C 1s, (b)N 1s and (c)Ti 2p in as-deposited ALD-TiO₂ film. The C 1s and N 1s peaks of ALD-TiO₂ film are undetectable.

Fig. 2. XRD patterns of as-deposited and annealed TiO₂ films. The PDA was carried out at 300-500 ºC in O₂. The anatase phase appears at temperature above 300 ºC.

Fig. 3. The CET values as a function of thickness of anatase-TiO₂ films on SiO₂/Si (100) and SiO₂/Si(111). The k values of Si(100) and Si(111) samples are estimated 35 and 32, respectively.

Fig. 4. The C-V characteristics of TaC-gated MOS capacitors with SiO₂, TiO₂, HfO₂ and Al₂O₃ dielectrics. The C-V curve of TiO₂ capacitor slightly shifts towards positive direction compared to SiO₂ one.

Fig. 5. The Vfb behaviors of SiO₂, TiO₂, HfO₂, Al₂O₃ and HSIO₃ [3] dielectrics. The value of the positive Vfb shift in high-k dielectric can be ordered as follows: Al₂O₃ (0.72 V) > HSIO₃ (0.36 V) > HfO₂ (0.29 V) > TiO₂ (0.08 V).

Fig. 6. Schematic band diagram of TaC/high-k/SiO₂/Si stack structure. The strength of the bottom interface dipole in high-k can be ordered as follows: Al₂O₃ > HSIO₃ > HfO₂ > TiO₂.

Fig. 7. Normalized Vfb versus ODA temperature for TiO₂ MOS capacitors with Pt and TaC gate electrodes. An inset graph shows C-V curves of Pt-gated MOS capacitors after FGA and ODA at 300 ºC. No difference of Vfb between Si(100) and Si(111) samples appears.

Fig. 8. Normalized Vfb of Pt-gated MOS capacitors as a function of annealing time. An inset graph shows C-V curves of capacitor in ODA 150 ºC. The change of Vfb in ODA at 150 ºC doesn’t saturate even at ODA times 200 min.

Fig. 9. The change of Vfb for TiO₂, HfO₂ [6] and HSIO₃ [6] dielectrics after ODA at 300 ºC and FGA at 500 ºC. The TiO₂ dielectric shows maximum positive Vfb shift and minimum negative Vfb shift after ODA and FGA, respectively.